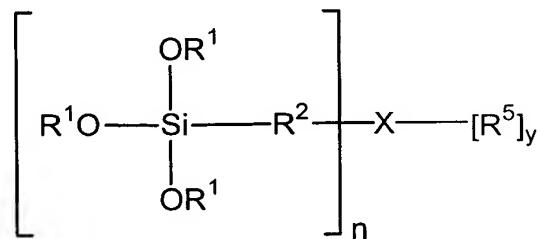


1. A method of treating a metal substrate, the method comprising:
 - applying a silane solution comprising a substantially hydrolyzed amino-silane and a substantially hydrolyzed sulfur-containing silane to at least a portion of a surface of the metal substrate; and
- 5 drying the solution on the metal substrate to form a coating having a thickness in the range from about 0.1 μm to about 1 μm thereon to treat the metal substrate.
2. The method of claim 1 further comprising, prior to applying the solution:
 - mixing an amino-silane and a sulfur-containing silane separately with an aqueous-based medium to substantially hydrolyze the amino-silane and the sulfur-containing silane; and
- 5 mixing the hydrolyzed amino-silane and the hydrolyzed sulfur-containing silane together to form the solution to be applied to the metal substrate.
3. The method of claim 2 wherein the amino-silane is a compound of the general formula I:



wherein:

5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

 each R², independently, is selected from the group consisting of

10 hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

 X is selected from the group consisting of



 wherein each R³, independently, is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups; and

20 R⁴ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

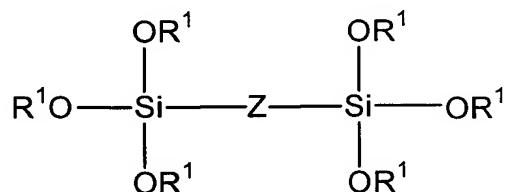
 R⁵ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

n is an integer selected from the group consisting of 1 and 2; and

y is (2-n).

4. The method of claim 2 wherein the amino silane is selected from the group consisting of bis(trimethoxysilylpropyl)ethylene diamine, bis(trimethoxysilylpropyl) amine, N-methyl-aminopropyltriethoxysilane, and combinations thereof.

5. The method of claim 2 wherein the sulfur-containing silane is a compound of the general formula II



wherein:

5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, alkynyl, and acetyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

Z is -Q-S_x-Q, wherein each Q, independently, is an aliphatic or aromatic group; and

x is an integer from 2 - 10.

6. The method of claim 2 wherein the sulfur-containing silane is selected

from the group consisting of bis(trimethoxysilylpropyl) disulfide, bis(trimethoxysilylpropyl) tetrasulfide, and a combination thereof.

7. The method of claim 1 wherein the solution comprises a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane in a range from about 1:4 to about 4:1 by volume.

8. The method of claim 1 wherein the solution comprises a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane of about 1:1 by volume.

9. The method of claim 1 wherein the solution is applied in an amount sufficient to form the coating to a thickness in the range from about 0.2 μm to about 0.6 μm .

10. The method of claim 1 wherein applying the coating solution to the metal substrate comprises dipping the metal substrate in the solution.

11. The method of claim 1 wherein the solution applied to the metal substrate further comprises a nanosize particulate material.

12. The method of claim 11 wherein the nanosize particulate material is selected from the group consisting of silica, zinc oxide, and combinations thereof.

13. The method of claim 11 wherein the nanosize particulate material has an average particle size of about 0.1 μm or less.

14. The method of claim 11 wherein the nanosize particulate material is silica and in a concentration range from about 10 ppm to about 1% by weight of the solution.

15. The method of claim 1 wherein the nanosize particulate material is silica and in a concentration range from about 50 ppm to about 1000 ppm of the solution.

16. A method of treating a metal substrate, the method comprising:

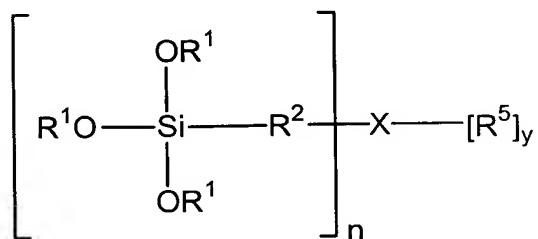
mixing an amino-silane and a sulfur-containing silane separately with an aqueous-based medium to substantially hydrolyze the amino-silane and the sulfur-containing silane;

5 mixing the hydrolyzed amino-silane, the hydrolyzed sulfur-containing silane, and a nanosize particulate material, having an average particle size of about 0.1 μm or less, together to form a silane solution comprising a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane in a range from about 1:4 to about 4:1 by volume,

10 applying the solution to at least a portion of a surface of the metal substrate in an amount sufficient to form a coating to a thickness in the range from about 0.1 μm to about 1 μm ; and

drying the solution on the metal substrate to form the coating thereon.

17. The method of claim 16 wherein the amino-silane is a compound of the general formula I



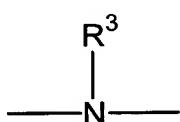
wherein:

5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

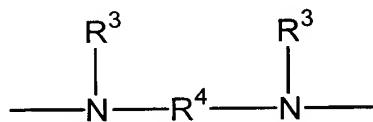
each R², independently, is selected from the group consisting of

10 hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

X is selected from the group consisting of



and



15 wherein each R³, independently, is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups; and

R⁴ is selected from the group consisting of hydrogen, substituted or

20 unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

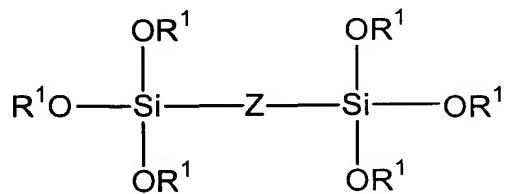
R⁵ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

25 n is an integer selected from the group consisting of 1 and 2; and

y is (2-n).

18. The method of claim 16 wherein the amino silane is selected from the group consisting of bis(trimethoxysilylpropyl)ethylene diamine, bis(trimethoxysilylpropyl) amine, N-methyl-aminopropyltriethoxsilane, and combinations thereof.

19. The method of claim 16 wherein the sulfur-containing silane is a compound of the general formula II



wherein:

5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, alkynyl, and acetyl groups and substituted or unsubstituted C₃-C₈ aryl and alkylaryl groups;

Z is -Q-S_x-Q, wherein each Q, independently, is an aliphatic or aromatic group; and

x is an integer from 2 - 10.

20. The method of claim 16 wherein the sulfur-containing silane is selected from the group consisting of bis(trimethoxysilylpropyl) disulfide, bis(trimethoxysilylpropyl) tetrasulfide, and a combination thereof.

21. The method of claim 16 wherein the solution applied to the metal comprises a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane of about 1:1 by volume.

22. The method of claim 16 wherein the solution is applied in an amount sufficient to form the coating to a thickness in the range from about 0.2 μm to about 0.6 μm .

23. The method of claim 16 wherein the nanosize particulate material is selected from the group consisting of silica, zinc oxide, and combinations thereof.

24. The method of claim 16 wherein the nanosize particulate material is silica and in a concentration range from about 10 ppm to about 1% by weight of the solution.

25. The method of claim 16 wherein the nanosize particulate material is silica and in a concentration range from about 50 ppm to about 1000 ppm of the solution.

26. A method of bonding a polymeric material to a metal substrate, the method comprising:

- applying a silane solution comprising a substantially hydrolyzed amino-silane and a substantially hydrolyzed sulfur-containing silane to at least a portion of a surface of the metal substrate;
- 5 drying the silane solution on the metal substrate to form a coating having a thickness in the range from about 0.1 μm to about 1 μm thereon; and
- applying an uncured polymeric material onto the surface of the metal substrate having the coating thereon and curing the polymeric material to bond 10 the polymeric material to the coated metal substrate.

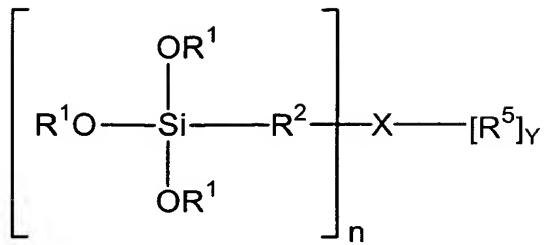
27. The method of claim 26 further comprising, prior to applying the solution:

mixing an amino-silane and a sulfur-containing silane separately with an aqueous-based medium to substantially hydrolyze the amino-silane and the sulfur-containing silane; and

- 5 mixing the hydrolyzed amino-silane and the hydrolyzed sulfur-containing silane together to form the solution to be applied to the metal substrate.

28. The method of claim 27 wherein the aqueous-based medium comprises water and alcohol.

29. The method of claim 27 wherein the amino-silane is a compound of the general formula I

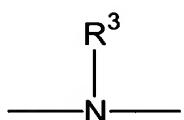


wherein:

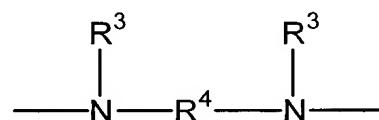
5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

each R², independently, is selected from the group consisting of
 10 hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

X is selected from the group consisting of



and



15 wherein each R³, independently, is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups; and

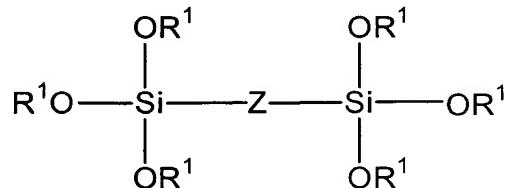
R⁴ is selected from the group consisting of hydrogen, substituted or

20 unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;
 R⁵ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

25 n is an integer selected from the group consisting of 1 and 2; and
 y is (2-n).

30. The method of claim 27 wherein the amino silane is selected from the group consisting of bis(trimethoxysilylpropyl)ethylene diamine, bis(trimethoxysilylpropyl) amine, N-methyl-aminopropyltriethoxysilane, and combinations thereof.

31. The method of claim 27 wherein the sulfur-containing silane is a compound of the general formula II



wherein:

5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, alkynyl, and acetyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

Z is -Q-S_x-Q, wherein each Q, independently, is an aliphatic or aromatic group; and

x is an integer from 2 - 10.

32. The method of claim 27 wherein the sulfur-containing silane is selected from the group consisting of bis(trimethoxysilylpropyl) disulfide, bis(trimethoxysilylpropyl) tetrasulfide, and a combination thereof.

33. The method of claim 26 wherein the solution comprises a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane in a range from about 1:4 to about 4:1 by volume.

34. The method of claim 26 wherein the solution comprises a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane of about 1:1 by volume.

35. The method of claim 26 wherein applying the solution to the metal substrate comprises dipping the metal substrate in the solution.

36. The method of claim 26 wherein the solution applied to the metal substrate further comprises a nanosize particulate material.

37. The method of claim 36 wherein the nanosize particulate material is selected from the group consisting of silica, zinc oxide, and combinations thereof.

38. The method of claim 36 wherein the nanosize particulate material has an average particle size of about 0.1 µm or less.

39. The method of claim 36 wherein the nanosize particulate material is silica and in a concentration range from about 10 ppm to about 1% by weight of the solution.

40. The method of claim 36 wherein the nanosize particulate material is silica and in a concentration range from about 50 ppm to about 1000 ppm of the solution.

41. The method of claim 26 wherein drying comprises heating the silane solution on the metal substrate to a temperature of at least about 60°C.

42. The method of claim 26 wherein the coating formed has a thickness in the range from about 0.2 µm to about 0.6 µm.

43. The method of claim 26 wherein curing comprises applying heat and pressure to the polymeric material and coated metal substrate to form a bond therebetween.

44. The method of claim 26 wherein the polymeric material is rubber.

45. A bonded tire cord prepared by the method of claim 26.

46. A method of bonding a polymeric material to a metal substrate, the method comprising:

mixing an amino-silane and a sulfur-containing silane separately with an aqueous-based medium to substantially hydrolyze the amino-silane and the

5 sulfur-containing silane;

mixing the hydrolyzed amino-silane, the hydrolyzed sulfur-containing silane, and a nanosize particulate material having an average particle size of about 0.1 μm or less, together to form a silane solution comprising a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane in a range

10 from about 1:4 to about 4:1 by volume,

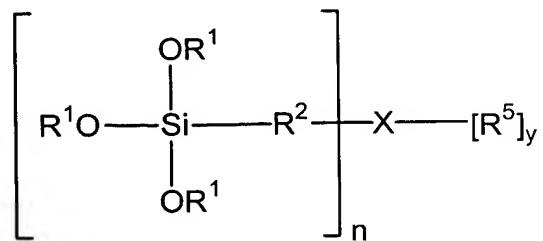
applying the solution to at least a portion of a surface of the metal substrate in an amount sufficient to form a coating to a thickness in the range from about 0.1 μm to about 1 μm ; and

drying the solution on the metal substrate to form the coating thereon;

15 applying an uncured polymeric material onto the surface of the metal substrate having the solution applied thereon; and

curing the polymeric material with heat and pressure to bond the polymeric material to the metal substrate.

47. The method of claim 46 wherein the amino-silane is a compound of the general formula I

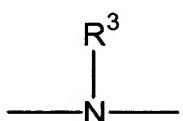


wherein:

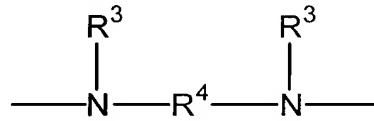
5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

each R², independently, is selected from the group consisting of
10 hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

X is selected from the group consisting of



and



15 wherein each R³, independently, is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups; and

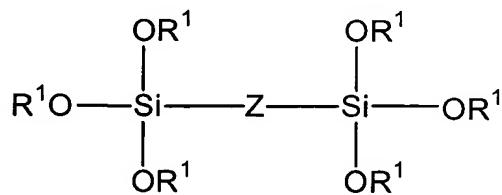
20 R⁴ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

R⁵ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

25 n is an integer selected from the group consisting of 1 and 2; and
y is (2-n).

48. The method of claim 46 wherein the amino silane is selected from the group consisting of bis(trimethoxysilylpropyl)ethylene diamine, bis(trimethoxysilylpropyl) amine, N-methyl-aminopropyltriethoxysilane, and combinations thereof.

49. The method of claim 46 wherein the sulfur-containing silane is a compound of the general formula II



wherein:

5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, alkynyl, and acetyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

Z is -Q-S_x-Q, wherein each Q, independently, is an aliphatic or aromatic group; and

10 x is an integer from 2 - 10.

50. The method of claim 46 wherein the sulfur-containing silane is selected from the group consisting of bis(trimethoxysilylpropyl) disulfide, bis(trimethoxysilylpropyl) tetrasulfide, and a combination thereof.

51. The method of claim 46 wherein the solution applied to the metal comprises a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane of about 1:1 by volume.

52. The method of claim 46 wherein the nanosize particulate material is selected from the group consisting of silica, zinc oxide, and combinations thereof.

53. The method of claim 46 wherein the nanosize particulate material is silica and in a concentration range from about 10 ppm to about 1% by weight of the solution.

54. The method of claim 46 wherein the nanosize particulate material is silica and in a concentration range from about 50 ppm to about 1000 ppm of the solution.

55. The method of claim 46 wherein the coating formed has a thickness in the range from about 0.2 μm to about 0.6 μm .

56. The method of claim 46 wherein the polymeric material is rubber.

57. A bonded tire cord prepared by the method of claim 46.

58. A tire cord comprising rubber, a metal substrate, and an adhesive film therebetween bonding the rubber to the metal substrate, the adhesive film formed from a dried solution comprising a substantially hydrolyzed amino-silane and a substantially hydrolyzed sulfur-containing silane and having a thickness in the range from about 0.1 μm to about 1 μm . .

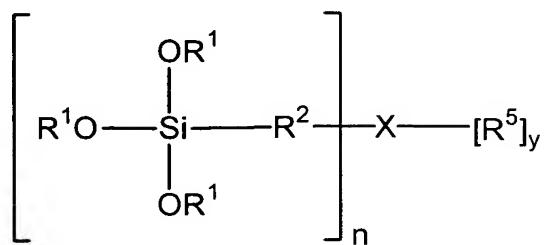
59. The tire cord of claim 58 wherein the rubber is selected from the group consisting of natural rubber, sulfur-cured rubber, peroxide-cured rubber, EPDM, NBR, SBR, and combinations thereof.

60. The tire cord of claim 58 wherein the substrate comprises a metal selected from the group consisting of zinc, steel, titanium, nickle, copper, tin, aluminum, cobalt, alloys thereof, and combinations thereof,

61. The tire cord of claim 58 wherein the solution comprises a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane of about about 1:4 to about 4:1 by volume.

62. The tire cord of claim 58 wherein the solution comprises a ratio of the hydrolyzed amino-silane to the hydrolyzed sulfur-containing silane of about 1:1 by volume.

63. The tire cord of claim 58 wherein the amino-silane is a substantially hydrolyzed compound of the general formula I

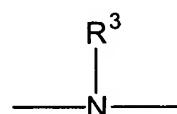


wherein:

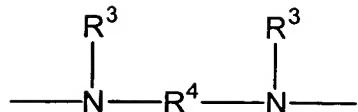
5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

each R², independently, is selected from the group consisting of 10 hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

X is selected from the group consisting of



15 and



wherein each R³, independently, is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups; and

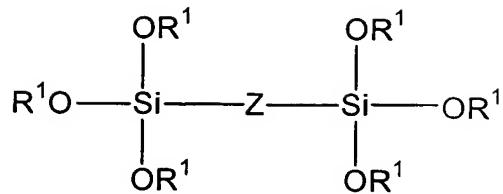
R⁴ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

R⁵ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

20 n is an integer selected from the group consisting of 1 and 2; and
y is (2-n).

64. The tire cord of claim 58 wherein the amino silane is a substantially hydrolyzed compound selected from the group consisting of bis(trimethoxysilylpropyl)ethylene diamine, bis(trimethoxysilylpropyl) amine, N-methyl-aminopropyltriethoxsilane, and combinations thereof.

65. The tire cord of claim 58 wherein the sulfur-containing silane is a substantially hydrolyzed compound of the general formula II



wherein:

5 each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, alkynyl, and acetyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

Z is -Q-S_x-Q, wherein each Q, independently, is an aliphatic or aromatic group; and

x is an integer from 2 - 10.

66. The tire cord of claim 58 wherein the sulfur-containing silane is a substantially hydrolyzed compound selected from the group consisting of bis(trimethoxysilylpropyl) disulfide, bis(trimethoxysilylpropyl) tetrasulfide, and a combination thereof.

67. The tire cord of claim 58 wherein the adhesive film has a thickness in the range from about 0.2 μm to about 0.6 μm.

68. The tire cord of claim 58 wherein the adhesive film further comprises a nanosize particulate material.

69. The tire cord of claim 68 wherein the nanosize particulate material is selected from the group consisting of silica, zinc oxide, and combinations thereof.

70. The tire cord of claim 68 wherein the nanosize particulate material has an average particle size of about 0.1 μm or less.

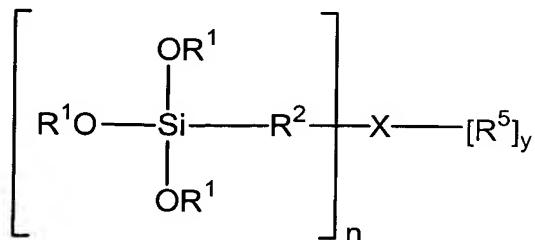
71. The tire cord of claim 68 wherein the nanosize particulate material is silica and in a concentration range from about 10 ppm to about 1% by weight in the adhesive film.

72. The tire cord of claim 68 wherein the nanosize particulate material is silica and in a concentration range from about 50 ppm to about 1000 ppm in the adhesive layer.

73. The tire cord of claim 58 wherein the rubber is substantially free of cobalt particles.

74. An metal treatment composition comprising a substantially hydrolyzed amino-silane, a substantially hydrolyzed sulfur-containing silane, and a nanosize particulate material.

75. The composition of claim 74 wherein the amino-silane is a substantially hydrolyzed compound of the general formula I

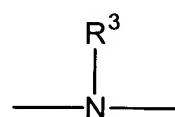


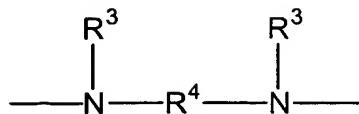
wherein:

5 each R^1 , independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic $\text{C}_1\text{-C}_{20}$ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted $\text{C}_3\text{-C}_{20}$ aryl and alkylaryl groups;

each R^2 , independently, is selected from the group consisting of
10 hydrogen, substituted or unsubstituted, straight, branched or cyclic $\text{C}_1\text{-C}_{20}$ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted $\text{C}_3\text{-C}_{20}$ aryl and alkylaryl groups;

X is selected from the group consisting of





wherein each R³, independently, is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups; and

R⁴ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

R⁵ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

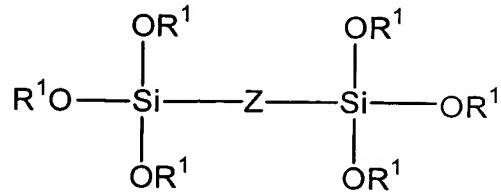
n is an integer selected from the group consisting of 1 and 2; and

y is (2-n).

76. The composition of claim 74 wherein the amino silane is a substantially hydrolyzed compound selected from the group consisting of bis(trimethoxysilylpropyl)ethylene diamine, bis(trimethoxysilylpropyl) amine, N-methyl-aminopropyltriethoxsilane, and combinations thereof.

77. The composition of claim 74 wherein the sulfur-containing silane is a

substantially hydrolyzed compound of the general formula II



5 wherein:

each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, alkynyl, and acetyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

10 Z is -Q-S_x-Q, wherein each Q, independently, is an aliphatic or aromatic group; and

x is an integer from 2 - 10.

78. The composition of claim 74 wherein the sulfur-containing silane is a substantially hydrolyzed compound selected from the group consisting of bis(trimethoxysilylpropyl) disulfide, bis(trimethoxysilylpropyl) tetrasulfide, and a combination thereof.

79. The composition of claim 74 wherein the hydrolyzed amino-silane and the hydrolyzed sulfur-containing silane are in a ratio in the range from about 1:4 to about 4:1 by volume.

80. The composition of claim 74 wherein the hydrolyzed amino-silane and the hydrolyzed sulfur-containing silane are in a ratio of about 1:1 by volume.

81. The composition of claim 74 wherein the nanosize particulate material is selected from the group consisting of silica, zinc oxide, and combinations thereof.

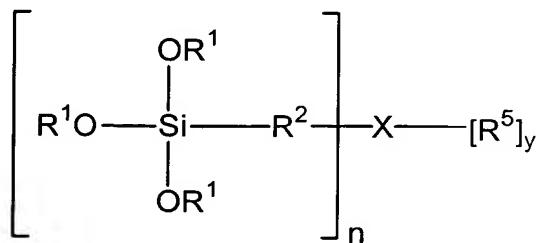
82. The composition of claim 74 wherein the nanosize particulate material has an average particle size of about 0.1 μm or less.

83. The composition of claim 74 wherein the nanosize particulate material is silica and in a concentration range from about 10 ppm to about 1% by weight in the composition.

84. The composition of claim 74 wherein the nanosize particulate material is silica and in a concentration range from about 50 ppm to about 1000 ppm in the composition.

85. A metal substrate comprising a coating having a thickness in the range from about 0.1 μm to about 1 μm on at least a portion of the surface thereof, the coating comprising a substantially hydrolyzed amino-silane and a substantially hydrolyzed sulfur-containing silane.

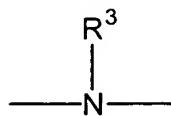
86. The metal substrate of claim 85 wherein the amino-silane is a substantially hydrolyzed compound of the general formula I



wherein:

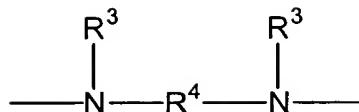
- 5 each R^1 , independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic $\text{C}_1\text{-C}_{20}$ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted $\text{C}_3\text{-C}_{20}$ aryl and alkylaryl groups;
- 10 each R^2 , independently, is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic $\text{C}_1\text{-C}_{20}$ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted $\text{C}_3\text{-C}_{20}$ aryl and alkylaryl groups;

X is selected from the group consisting of



15

and



wherein each R³, independently, is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups; and

R⁴ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

R⁵ is selected from the group consisting of hydrogen, substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, and alkynyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

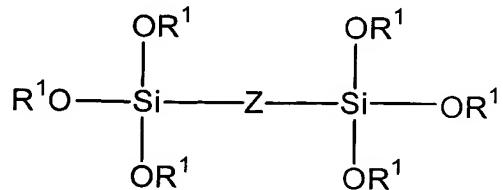
n is an integer selected from the group consisting of 1 and 2; and

y is (2-n).

87. The metal substrate of claim 85 wherein the amino silane is a substantially hydrolyzed compound selected from the group consisting of bis(trimethoxysilylpropyl)ethylene diamine, bis(trimethoxysilylpropyl) amine, N-

methyl-aminopropyltriethoxysilane, and combinations thereof.

88. The metal substrate of claim 85 wherein the sulfur-containing silane is a substantially hydrolyzed compound of the general formula II



5 wherein:

each R¹, independently, is selected from the group consisting of substituted or unsubstituted, straight, branched or cyclic C₁-C₂₀ alkyl, alkenyl, alkynyl, and acetyl groups and substituted or unsubstituted C₃-C₂₀ aryl and alkylaryl groups;

10 Z is -Q-S_x-Q, wherein each Q, independently, is an aliphatic or aromatic group; and

x is an integer from 2 - 10.

89. The metal substrate of claim 85 wherein the sulfur-containing silane is a substantially hydrolyzed compound selected from the group consisting of bis(trimethoxysilylpropyl) disulfide, bis(trimethoxysilylpropyl) tetrasulfide, and a combination thereof.

90. The metal substrate of claim 85 wherein the hydrolyzed amino-silane and the hydrolyzed sulfur-containing silane are in a ratio in the range from

about 1:4 to about 4:1 by volume.

91. The metal substrate of claim 85 wherein the hydrolyzed amino-silane and the hydrolyzed sulfur-containing silane are in a ratio of about 1:1 by volume.

92. The metal substrate of claim 85 wherein the coating further comprises a nanosize particulate material.

93. The metal substrate of claim 92 wherein the nanosize particulate material is selected from the group consisting of silica, zinc oxide, and combinations thereof.

94. The metal substrate of claim 92 wherein the nanosize particulate material has an average particle size of about 0.1 μm or less.

95. The metal substrate of claim 92 wherein the nanosize particulate material is silica and in a concentration range from about 10 ppm to about 1% by weight in the composition.

96. The metal substrate of claim 92 wherein the nanosize particulate material is silica and in a concentration range from about 50 ppm to about 1000 ppm in the composition.